Saha Equation

The Saha equation gives a relationship between free particles and those bound in atoms. To derive the Saha equation, choose a consistent set of energies. Also choose $E = 0$ when the electron velocity is zero, so $E = -I$ for $n = 1$. Ignore the energy of the higher n levels, since if an electron has enough energy to reach $n = 2$, it needs only 1/4 more energy to ionize completely, by the Bohr energy equation

$$E = \frac{Z}{n^2}(-13.6 \text{ eV}). \qquad (1)$$

Let $S(N_e, N)$ be the probability that the gas has N_e electrons out of N particles in a given ensemble. The partition functions for each class of particles are

$$Z_e \equiv \sum_n e^{-E(n)/(kT)} \qquad (2)$$

$$Z_p \equiv \sum_n e^{-E(n)/(kT)} \qquad (3)$$

$$Z_H \equiv \sum_n e^{-E(n)/(kT)} \qquad (4)$$

So the probability function, assuming indistinguishable particles, is

$$S(N_e, N) = \frac{Z_e^{N_e}}{N_e!}\frac{Z_p^{N_p}}{N_p!}\frac{Z_H^{N_H}}{N_H!}. \qquad (5)$$

The sums in the partition functions are actually integrals, since the particles have a continuous momentum distribution. Therefore, for Z_e and Z_p

$$Z_i = \int g_i e^{-[p^2/(2m)]/(kT)} \frac{d^3\mathbf{x}\, d^3\mathbf{p}}{h^3}, \qquad (6)$$

where i is either e or p. Using

$$d^3\mathbf{p} = 4\pi p^2\, dp \qquad (7)$$

gives

$$Z_i = \frac{4\pi g_i}{h^3} \int d^3\mathbf{x} \int_0^\infty p^2 e^{-[p^2/(2m)]/(kT)}\, dp. \qquad (8)$$

Let

$$y^2 \equiv \frac{p^2}{2mkT} \tag{9}$$

$$2y\,dy = \frac{p}{mkT}\,dp \tag{10}$$

$$p\,dp = 2mkTy\,dy, \tag{11}$$

then

$$\begin{aligned} Z_i &= \frac{4\pi g_1 V}{h^3}(2mkT)^{1/2}\int_0^\infty (2mkT)y^2 e^{-y^2}\,dy \\ &= 4\frac{\pi g_1 V}{h^3}(2mkT)^{3/2}\int_0^\infty y^2 e^{-y^2}\,dy \\ &= 4\frac{\pi g_1 V}{h^3}(2mkT)^{3/2}\frac{\sqrt{\pi}}{4} \\ &= \frac{g_i V}{h^3}(2\pi mkT)^{3/2}. \end{aligned} \tag{12}$$

Since electrons and protons are both fermions,

$$g_e = g_p = 2, \tag{13}$$

and

$$Z_e = \frac{2V}{h^3}(2\pi m_e kT)^{3/2} \tag{14}$$

$$Z_p = \frac{2V}{h^3}(2\pi m_p kT)^{3/2}. \tag{15}$$

The derivation is identical for Z_H, except that the binding energy term is carried through and $g_H = 4$, resulting in

$$Z_H = \frac{4V}{h^3}(2\pi m_H kT)^{3/2} e^{I/(kT)}. \tag{16}$$

We want to find the most probable state, so we should differentiate (2). However, because $\ln x$ is monotonic, $\ln f(x)$ will have a maximum at the same place as *f*(*x*). Taking the log of (5) and using Stirling's approximation and $n \gg 1$

$$\ln n! \approx n \ln n - n, \tag{17}$$

the result is

$$\ln S = N_e \ln Z_e + N_p \ln Z_p + N_H \ln Z_H - N_e \ln N_e + N_e - N_p \ln N_p + N_p - N_H \ln N_H + N_H. \quad (18)$$

Using the definitions

$$N_e = N_p \quad (19)$$

$$N_H = N - N_e \quad (20)$$

and taking the derivative of (18)

$$\frac{d(\ln S)}{dN_e} = \ln Z_e + \ln Z_p - \ln Z_H - \ln N_e - \ln N_e + \ln(N - N_e) = 0. \quad (21)$$

The resulting relationship is

$$\frac{Z_e Z_p}{Z_H} = \frac{N_e^2}{N - N_e}. \quad (22)$$

Plugging in (14)-(16) into (22),

$$\frac{\left[\frac{2V(2\pi m_e kT)^{3/2}}{h^3}\right]\left[\frac{2V(2\pi m_p kT)^{3/2}}{h^3}\right]}{\left[\frac{4V(2\pi m_H kT)^{3/2}}{h^3}\right] e^{I/(kT)}} = \frac{N_e^2}{N - N_e}. \quad (23)$$

Canceling and taking $m_H \approx m_p$,

$$\frac{V}{h^3}(2\pi m_e kT)^{3/2} e^{-I/(kT)} = \frac{N_e^2}{N - N_e} \quad (24)$$

$$\frac{(2\pi m_e kT)^{3/2} e^{-I/(kT)}}{h^3} = \frac{n_e^2}{n - n_e}. \quad (25)$$

Defining the ionization fraction as

$$X \equiv \frac{n_e}{n}, \quad (26)$$

then

$$\frac{X^2}{1 - X} = \frac{1}{nh^3}(2\pi m_e kT)^{3/2} e^{-I/(kT)}. \quad (27)$$

SEE ALSO: Ionization